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(71) Applicant (for all designated States except US): **HYCAIL B.V. [NL/NL]**; Industrieweg 24-1, NL-9804 TG Noordhorn (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **SÖDERGARD, Anders [FI/NL]**; M. L. Kingstraat 20, NL-9728 WJ Groningen (NL).

(74) Agent: **PRINS, A.W.**; c/o Vereenigde, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).

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**WO 02/076232 A1**

(54) Title: **BIODEGRADABLE GUM BASE SHOWING IMPROVED PROPERTIES**

(57) Abstract: The invention is directed to a chewing gum, comprising a gum base and at least one other conventional chewing gum component, said chewing gum comprising as gum base at least one branched polymer mainly based on biodegradable and/or hydrolyzable ester groups.

Title: Biodegradable gum base showing improved properties

This invention relates to a chewing gum containing a gum base and/or additives from biodegradable resources showing improved softness and chewability with regard to earlier described formulations based on biodegradable polymers. It is known that chewing gum formulations can be  
5 made from biodegradable, environmentally more acceptable polymers than the conventional non-biodegradable polymers used as gum base in chewing gums. Examples of this have been described, for instance, in US-A-5 672 367 and EP-A-0 711 506, where aliphatic polyesters were used, in US-A-6 153 231, where oxazoline or urethane consisting copolymers of poly(lactic acid) were  
10 disclosed, and in WO-A-99/39588, where bacterial polyhydroxyalkanoates having side chains of C<sub>4</sub> to C<sub>30</sub> were used in chewing gum formulations.

A further example of chewing gums containing biodegradable gum bases prepared from aliphatic polyesters is described in WO-A-00/19837. These disclosed gum bases based on poly(D,L-lactic acid) and copolymers thereof do,  
15 however, have need of plasticizing agents in order to obtain the softness and chewability required in a gum base. Furthermore, a glass transition temperature of 35.8 °C is presented for a pure poly(D,L-lactic acid) with a viscosity-average molar mass of 42 200 g/mol. It is apparent that a pure poly(D,L-lactic acid) of this molar mass, without any kind of plasticizing  
20 component present, cannot show a softening temperature that low, as it is commonly known that these kind of polymers have a glass transition temperature higher than that.

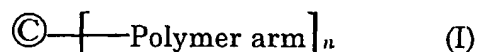
EP-A-0 882 751 discloses a method for preparing a biodegradable aliphatic polyester in the presence of minute amounts of co-catalysts  
25 comprising glycerol or butyrolactone. The polyester prepared showed lower melt viscosities than a polymer prepared without the co-catalyst at the preferred molding temperatures around 180 °C.

In the present invention, however, a gum base is prepared by making branched or star-shaped polymers with several polyester branches or

arms attached to a central polyfunctional compound, thus, surprisingly, resulting in the gum base having improved softness and chewability. Further improvements in the current invention are the use of certain starting compounds or preparation conditions giving the final chewing gum additional functional properties.

The present invention relates to a degradable gum base, where special properties are achieved by the choice of starting compounds and/or preparation conditions during the synthesis of the polymer or during post-polymerization processing.

The polymers used according to the present invention are branched polymers with several polyester branches or arms polymerized onto a polyfunctional compound with desired properties, as schematically shown in Formula (I).



wherein,  
 C = central polyfunctional; and  
 n = polymer arms attached to C.

A polymer according to the invention can be prepared from the ring-like ester, such as L,L-lactide, D,D-lactide, *rac*-lactide, *meso*-lactide or mixtures thereof, glycolide, trimethylene carbonate, lactones, such as  $\beta$ -propiolactone,  $\delta$ -valerolactone,  $\epsilon$ -caprolactone, or other corresponding cyclic compound like cyclic amides. The polymer can also be prepared by condensation reaction from a hydroxy acid, such as lactic acid, glycolic acid, amino acids, or from monomeric units of diols and diacids. Such a polymer can for instance be used in the form of block copolymers, random copolymers, graft-copolymers, or as mixtures of two or more homo- and/or copolymers. The invention can be described as a concept where the starting compounds in the

polymerization will affect a larger number of different properties, of which some are described below:

1. The initiator determines the structure of the polymer, i.e. the degree of branching, which reflects on the viscoelastic properties of the gum base, which in turn determines the chewing properties of the chewing gum (examples on such compounds are decanol, pentaerythritol, dipentaerythritol).
2. The type of starting materials used can have an impact on other properties related to the performance and appearance of the chewing gum. Examples on such properties are the sweetening effect, compatibility with other ingredients, and taste retention (examples on such compounds are decanol, sorbitol, inositol).
3. The choice of starting material and/or preparation conditions or post-polymerization processing may offer benefits in the view of health aspects for instance by equipping the gum base with for instance antibacterial effect (lactic acid and lactones are known antibacterial substances) or other effects (examples on such compounds are lactones, xylitol, organic acids, hydroxylapatite).
4. The starting material, ways of preparation and processing conditions have a significant impact on the hydrolytic stability of the polymer used in the gum base, which will affect the compostability and enable the removal of undesired chewing gum from, for example, clothes, furniture, streets, and floors. Degradation enhancing compounds can be compounds increasing the hydrophilicity (for instance anhydrides or carboxylic acid compounds) or compounds catalyzing the rate of hydrolysis (for instance amino or amido compounds).

The polyfunctional compounds according to present invention typically contain three or more hydroxyl groups, such as trimethylolethane, trimethylolpropane, butanetriol, phloroglucinol, erythritol, pentaerythritol, or dipentaerythritol. Naturally occurring polyfunctional compounds of sugars of mono-, di-, or trisaccharides of hexoses or pentoses, or maltitol, sorbitol,

mannitol, xylitol, inositol, or such, can optionally be used. The polyfunctional compound can be used alone or in any combination with other homo- or polyfunctional compounds. It should, however, be understood that current invention should not be limited to the few polyfunctional compounds

5 mentioned as examples herein, but should be considered in a broader sense within the spirit and scope of present invention. For a person skilled in the art it will be apparent that, for instance, the polyfunctional compound does not have to be a hydroxyl containing compound, but can also consist of other initiating species, such as, for example, amino groups.

10 In a preferred embodiment of the current invention a star-shaped copolymer or block copolymer of a lactide and one or more other cyclic esters, such as glycolide, trimethylene carbonate, lactones, such as  $\beta$ -propiolactone,  $\delta$ -valerolactone,  $\epsilon$ -caprolactone, or lactones of larger size, or a mixture of two or more polymers, with at least one polymer containing lactide, is used in the  
15 gum base. Preferably a system containing at least 50 mol % lactide, more particularly at least 65 mol % lactide, is used.

The polymerization can be done by any conventional polymerization technique, such as, for example, polymerization in bulk or solution, generally in the presence of a proper amount of suitable polymerization catalyst.

20 A chewing gum typically consists of a water-soluble bulk part, a water-insoluble gum base, and flavoring components. The water-soluble part of the chewing gum comprises of, for example plasticizers, sweeteners and combinations thereof. Plasticizers, such as glycerin, lecithin and combinations thereof, are conventionally added for improving the softness and chewability of  
25 the water-insoluble gum base. It was, however, surprisingly noticed that in the current invention usage of plasticizers are not necessary in order to obtain the chewability and mouthfeel required in chewing gums. Plasticizers may optionally be used in the gum base formulations described herein.

The water-soluble sweeteners consists of, for example, saccharide  
30 containing components conventionally used in chewing gum, dried invert

sugar, sucrose, dextrose, maltose, fructose, levulose, galactose and the like, alone or in combination with other sweeteners. Sugarless sweeteners, including, for instance, sugar alcohols such as sorbitol, mannitol, xylitol, maltitol, hydrogenated starch hydrolysates and the like, are also commonly  
5 used, alone or in combination with other sweeteners. Other typical sweeteners, such as, for example, aspartame, acesulfame, and saccharide, can be used alone or in combination.

A chewing gum can further contain about 0.1 to 10% flavoring components. The flavoring components may include, for example, oils from  
10 plants and fruits, such as citrus oil, fruit extracts, peppermint oil, spearmint oil, clove oil, aniseed oil, alone or as mixtures with other flavor inducing agents.

Furthermore, fillers, such as magnesium and calcium carbonate, kaolin, tricalcium phosphate, talc, wood fiber, apple fiber, zein, gluten, casein,  
15 can optionally be added to the chewing gum. Natural organic fillers are preferably used in current invention.

Additional components, such as colorants, medical components, mouth conditioners, and antioxidants, can also be added to the chewing gum, either during the polymerization or afterwards.

20 By no way of limiting the present invention, explanatory examples will be given in the following. Standard laboratory procedures were used in all chemical handling, purification, drying, and synthesis. Calculations known in the art for obtaining a polymer of a certain number-average molar mass and/or copolymer composition were used. The polymerization experiments were  
25 performed under an inert atmosphere in an electrically heated Brabender W 50 E mixer, unless otherwise stated. Usual polymerization conditions were as follows:

- Polymerization temperature: 140-170 °C.
- Polymerization time: 30-240 min.
- 30 – Rotationspeed of the mixer: 15 rpm.

– 0.05 wt % stannous 2-ethylhexanoate was used as catalyst  
 – Amount of monomers and initiators were varied, depending on the calculated number-average molar mass and/or copolymer composition of the resulting polymers, so that total amount put in the mixer was 40 g.

5 A GPC (Gel Permeation Chromatography) apparatus was used for molar mass measurements. The monomer conversion, number-average molar mass, and copolymer composition were determined by NMR technique. Differential Scanning Calorimetry (DSC) was used for measuring the thermal properties, e.g. the glass transition temperature ( $T_g$ ).

10 While the invention has been described in detail with respect to specific preferred embodiments thereof, it will be appreciated that those skilled in the art, upon reading and understanding of the foregoing will readily envision modifications and variations to the preferred embodiments which are nonetheless within the spirit and scope of the invention and of the claims.

15

### EXAMPLE 1

An amorphous, non-crystallizable copolymer of (50/50)*rac*-lactide was prepared by ring-opening polymerization in the melt by using different hydroxyl compounds as initiators. The initiators and some polymer properties  
 20 are listed in Table 1.

**Table 1.** Examples on different initiators in the preparation of gum bases based on *rac*-lactide.

Experiment No	Initiator	$M_w$ g/mol	$M_n$ g/mol	$T_g$ °C
1	1-Decanol	33 500	20 000	44
2	Phloroglucinol	33 800	19 900	49
3	Inositol	16 400	12 600	44
4	Dipentaerythritol	21 600	18 300	43

## EXAMPLE 2

Star-shaped copolymers of lactide and  $\epsilon$ -caprolactone were prepared by ring-opening polymerization in the melt by using a star-shaped poly( $\epsilon$ -caprolactone) with pentaerythritol core as macroinitiator. The star-shaped polymeric gum bases, with no components added, showed a chew feel similar to the one of a conventional commercially available chewing gum. The conditions during the experiments and the results from the series are shown in Table 2.

Table 2. Examples on gum bases consisting of branched copolymers of lactide and  $\epsilon$ -caprolactone.

Experiment No	Lactide	$\epsilon$ -CL / Lactide ratio	$M_w$ g/mol	$M_n$ g/mol	$T_g$ °C
5	<i>Rac</i>	37 / 63	29 600	25 900	-20
6	L,L	42 / 58	26 400	23 900	- *)
7	<i>Rac</i>	54 / 46	19 300	17 200 **)	-23
8	<i>Rac</i>	32 / 68	43 700	32 600 **)	-13
9	<i>Rac</i>	22 / 78	67 500	43 000 **)	+2

\*) Not detected; DSC showed  $T_m = 150$  °C,  $\Delta H = 33$  J/g

\*\*) Based on NMR

## EXAMPLE 3

Star-shaped random copolymers consisting of  $\epsilon$ -caprolactone and (50/50)*rac*-lactide were prepared by ring-opening polymerization, initiated by pentaerythritol, in the melt. The polymer characteristics are presented in Table 3.

**Table 3.** Examples on gum bases consisting of branched random copolymers of *rac*-lactide and  $\epsilon$ -caprolactone.

Experiment No	$\epsilon$ -CL / Lactide ratio	$M_n$ g/mol *)	$M_w / M_n$	$T_g$ °C
10	3 / 97	17 500	1.34	+45
11	8 / 92	16 700	1.35	+40
12	14 / 86	15 800	1.42	+35

\*) Based on NMR

5

#### EXAMPLE 4

800 g 88% L-lactic acid was dried and condensation polymerized in the presence of 0.2 wt % tin(II) oxide at 180 °C in a standard laboratory rotary evaporator unit under reduced pressure and argon flow until the poly(L-lactic acid) had a  $M_n$  of 1 900 g/mol ( $M_w/M_n = 3.12$ ). The poly(L-lactic acid) was then further linked with 96 g of a hydroxyl-terminated star-shaped poly( $\epsilon$ -caprolactone) with a pentaerythritol core at 195 °C ( $p = 5$  mbar) in the laboratory rotary evaporator unit, resulting in a star-shaped copolymer with  $M_n = 7\,400$  g/mol. DSC showed a  $T_g = -22$  °C and  $T_m = 130$  °C.

15

#### EXAMPLE 5

800 g of 88% L-lactic acid was dried and condensation polymerized in the presence of 20 g succinic acid and 0.1 wt % stannous 2-ethylhexanoate at 180 °C in a standard laboratory rotary evaporator unit under reduced pressure until the poly(L-lactic acid) had a  $M_w$  of 3 800 g/mol. 40 g of the brittle poly(L-lactic acid) was further linked with 40 g of a hydroxyl-terminated star-shaped poly( $\epsilon$ -caprolactone) with a pentaerythritol core at 180 °C ( $p = 25$  mbar) in the laboratory rotary evaporator unit until the resulting soft star-shaped multi-branched copolymer reached a  $M_w = 40\,600$  g/mol.

## EXAMPLE 6

88% D,L-lactic acid was dried and condensation polymerized in the presence of 0.1 wt % stannous 2-ethylhexanoate at 180 °C in a standard laboratory rotary evaporator unit under reduced pressure until the poly(D,L-lactic acid) had a  $M_w$  of 3 000 g/mol ( $M_w/M_n = 2.70$ ). The brittle poly(D,L-lactic acid) was further linked with 117.0 g of a hydroxyl-terminated star-shaped poly( $\epsilon$ -caprolactone) with a pentaerythritol core at 180 °C ( $p = 23$  mbar) in the laboratory rotary evaporator unit, resulting in a star-shaped copolymer with  $M_w = 8$  500 g/mol. Without the addition of any plasticizing agents this soft copolymer showed a  $T_g$  of 6 °C, as determined by DSC.

## EXAMPLE 7

Star-shaped random copolymers consisting of  $\epsilon$ -caprolactone and (50/50) *rac*-lactide were prepared by ring-opening polymerization, initiated by pentaerythritol, in the melt. The amount of residual lactide available for hydrolysis (eventually into lactic acid) could be determined by the choice of polymerization time (Table 4).

Table 4. The amount of residual lactide as a function of polymerization time.

Experiment No *)	Residual lactide at different polymerization times mol % **)		
	30 min	60 min	90 min
10	7.0	5.6	3.6
11	10.7	3.9	2.7
12	4.3	2.4	1.8

\*) Experiment no. from Example 3; \*\*) Based on NMR

## EXAMPLE 8

A star-shaped copolymer of *rac*-lactide and  $\epsilon$ -caprolactone was prepared in the same manner as in Example 2 and the gum base was tested for rheological properties. The gum base, with no components added, showed rheological properties comparable to a conventional gum base.

Claims

1. Chewing gum, comprising a gum base and at least one other conventional chewing gum component, said chewing gum comprising as gum base at least one branched polymer mainly based on biodegradable and/or hydrolyzable ester groups.
- 5 2. Chewing gum, comprising a gum base and at least one chewing gum additive, said chewing gum comprising as chewing gum additives at least one branched polymer mainly based on biodegradable and/or hydrolyzable ester groups.
3. Chewing gum of claim 1 or 2, comprising as said at least one  
10 branched polymer a star-shaped biodegradable polymer with several branches or arms attached to a central polyfunctional compound.
4. Chewing gum of claim 3, wherein the said polyfunctional compound is based on one or more compounds having at least 3 hydroxyl or amino groups.
- 15 5. Chewing gum of claim 1, wherein the said at least one branched polymer is based on one or more cyclic esters (such as L,L-lactide, D,D-lactide, *rac*-lactide, *meso*-lactide,  $\epsilon$ -caprolactone, glycolide or rings of other size), cyclic carbonates (such as trimethylene carbonate), cyclic amides (such as caprolactam) by ring-opening polymerization.
- 20 6. Chewing gum of claim 5, wherein the said at least one branched polymer is made from one or more from one or more diol/diacid combinations, or from hydroxy acids, such as lactic acid and glycolic acid, or from amino acids by polycondensation.
7. Chewing gum compound of claim 1 where the starting compounds  
25 give the final formulation one or several functions, such as softening temperature, viscoelasticity, taste, compatibility or degradability.

8. Chewing gum compound of claim 1 where the processing conditions gives the final formulation one or several functions, such as softening temperature, viscoelasticity, taste, compatibility or degradability.

## INTERNATIONAL SEARCH REPORT

tional Application No

PCT/NL 02/00199

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 A23G3/30

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 711 506 A (UNIV GRONINGEN) 15 May 1996 (1996-05-15) cited in the application the whole document ----	1-8
X	WO 00 19837 A (LI WEISHENG ; WRIGLEY W M JUN CO (US)) 13 April 2000 (2000-04-13) the whole document ----	1-8
A	EP 0 882 751 A (KOBE STEEL EUROP LTD ; KOBE STEEL LTD (JP)) 9 December 1998 (1998-12-09) the whole document -----	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Weber, G

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0711506	A	15-05-1996	NL 9401703 A	01-05-1996
			EP 0711506 A2	15-05-1996
			FI 954867 A	15-04-1996
			JP 8196214 A	06-08-1996
			US 5672367 A	30-09-1997
<hr/>				
WO 0019837	A	13-04-2000	WO 0019837 A1	13-04-2000
			AU 9678298 A	26-04-2000
			EP 1133240 A1	19-09-2001
<hr/>				
EP 0882751	A	09-12-1998	EP 0882751 A2	09-12-1998
			JP 11049851 A	23-02-1999
			US 5886093 A	23-03-1999
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